CERAMIC COATINGS FOR COMPONENTS
EXPOSED TO COAL-GAS ENVIRONMENTS:
A REVIEW

by

Robert Swaroop

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Materials Science Division

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ABSTRACT

The corrosive and erosive environments at high tempera-
tures and pressures in coal gasifiers impose severe require-
ments on the alloys of fabrication. A concise review of the
application of ceramic coatings to resist coal-gas environ-
ments has been conducted.

The purpose of this review is to explore suitable ceramic
or cermet materials that may resist or retard the degradation
of metal components and to summarize the state of the art of
various methods of producing such coatings.

I. INTRODUCTION

A concise review of the application of ceramic coatings in coal-gasi-
fication (liquefaction) environments has been conducted. The objectives are
to summarize the state of the art of the various coating systems and to sug-
gest adequate ceramic coatings (or coating systems) that can resist or retard
the degradation of components used in coal-gasification plants. Also, the
various methods of producing ceramic coatings are discussed, and suggestions
are made as to economical and feasible techniques of production or the devel-
opment of such techniques.

Coatings to protect structural materials against oxidation and sulfi-
dation (hot corrosion) at high temperatures have become significant in recent
years. In the past, superalloys (Ni- or Co-base) containing up to 20% chromium
were used where both strength and oxidation resistance were required, as in
the turbine section of jet engines. In recent years, stronger superalloys
have been developed by increasing the aluminum and titanium content to form
strengthening γ' precipitates at the expense of chromium content.[1] Unfortu-
nately, these superalloys have significantly poorer hot-corrosion resistance
than the 20% chromium alloys. To combat this problem, coatings, primarily
monoaluminides, have been produced by diffusion into the substrate alloys.[2,3]
These coatings provide improved oxidation and sulfidation resistance and have
been used successfully in some applications, even up to 1200°C turbine inlet
temperatures.

Other developments that have led to increased attention to high-
temperature coatings are glide reentry and hypersonic vehicles. Refractory
metal alloys of Cb, Ta, Mo, and W provided excellent oxidation resistance to
1370°C. The performance of these alloys was improved by disilicide and mono-
aluminide coatings[4,5] that are capable of protecting the alloys to 1600°C.

The presently proposed energy-conversion systems, especially in the coal-gasification/liquefaction processes, impose quite severe demands on the fabrication of metals and alloys. Temperatures as high as 1600°C and pressures as high as 1500 psig could be realized in the corrosive-erosive environments of the gaseous mixtures, as shown in Table I. This table includes the expected gaseous compositions in the gasifier portion of five pilot plants that will produce high Btu gas.[6] The most corrosive component is hydrogen sulfide. The thermodynamic equilibria among these gases at 1000°C will produce simultaneous chemical reactions and a quasi-equilibrium system that will contain at least 20 species in the gasifier. The computed equilibrium partial pressures of some of these species are shown in Table II. These computations were performed on the basis of the average composition of the gaseous mixture that will be produced in the IGT-HYGAS pilot plant. The actual range of compositions for all plants, as indicated in Table I, will produce partial pressures of oxygen between 10^{-15} and 10^{-17} atm and sulfur between 10^{-6} and 10^{-9} atm at 1000°C.

TABLE I. Approximate Compositions of Raw Gases Leaving Gasifiers for Several Processes (mole %)[6]

Component	Bi-Gas	CO_2 Acceptor	HYGAS- Oxygen	HYGAS- Air	Self- agglomerating	Synthane
CO	22.9	14.1	18.0	13.5	26.0	10.5
CO_2	7.3	5.5	18.5	12.7	5.0	18.2
H_2	12.7	44.6	22.8	16.6	48.0	17.5
H_2O	48.0	17.1	24.4	18.3	14.0	37.1
CH_4	8.1	17.3	14.1	8.4	6.0	15.4
C_2H_6	-	0.37	0.5	0.6	-	0.5
H_2S	0.7	0.03	0.9	0.8	0.5	0.3
NH_3	-	0.8	-	-	-	-
N_2	0.3	0.2	0.3	28.9	0.5	0.5
Other	-	-	0.5	0.2	-	-

TABLE II. Equilibrium Partial Pressures[a] of Various Species[b] at 1026°C (1880°F)

Species	P_x, atm	Species	P_x, atm
O_2	1.6×10^{-15}	COS	1.3×10^{-2}
S_2	2.6×10^{-6}	CO_2	5.7
CO	20.9	H_2O	12.1
H_2	26.4	H_2S	0.49
S	4.0×10^{-9}	HS	3.4×10^{-5}
SO	2.5×10^{-8}	CS	8.2×10^{-6}
SO_2	1.4×10^{-7}	CS_2	6.7×10^{-6}
SO_3	7.2×10^{-16}	CH_4	2.3
		C_2H_6	3×10^{-4}

[a]At a total pressure of 68 atm.

[b]Using HYGAS-raw gas composition (Table I).

II. SULFIDATION

Zalenko and Simkovich[7] and Farber and Ehrenberg[8] investigated the sulfidation behavior of iron-base alloys in the partial pressures of H_2S-H_2 mixtures. The low chromium content iron-base alloys produce FeS with a minor amount of CrS in solid solution with FeS. The high chromium iron-base alloys produce a multiphase scale consisting of FeS and Cr_2S_3 or iron-chromium-sulfide spinel.[9,10]

Mrowec and Werber[11] and Hancock[12] studied the behavior of Ni-base alloys in H_2S and SO_2 environments. They observed that, in an SO_2 atmosphere, a continuous film of Cr_2O_3 is formed, and the layer is protective against additional sulfidation, provided the alloy contained sufficient chromium so that the subscale does not become denuded of chromium. However, in an H_2S environment, a continuous film of CrS is formed, provided sufficient chromium is present to maintain the protective film. Furthermore, it was concluded from their results that, in the temperature range of 500-900°C with a chromium content of <20%, a protective film was not always possible and corrosion proceeded by the diffusion of nickel ions outward and sulfur ions inward. In alloys that had a chromium content >20%, the corrosion was restricted and governed only by metal-ion diffusion. Sulfidation corrosion is also strongly influenced by the aluminum content of the alloy; the higher the Al content the lower the sulfidation rate.[7] A protective layer of Al_2S_3 or a mixture of Al_2S_3 and chromium sulfides has been observed to retard sulfidation attack.

In coal gasifiers, sulfidation is expected to be quite severe, since the sulfur activities will be substantially higher (Tables I and II) than those studied by other investigators.[7-12] In general, the sulfides formed by the attack of H_2S, SO_2, or SO_3 have low melting temperatures and, as a consequence, may actually fuse on the alloy surface. The sulfide films are also known to be porous, nonadherent, and discontinuous, thus excluding them as prospective candidates for protective coatings on alloy surfaces.[7-12]

III. OXIDATION

The oxidation resistance of iron- or nickel-base alloys increases as the chromium content of the alloy increases. In general, the conclusion is that adherent protective layers of $NiO \cdot Cr_2O_3$ and Cr_2O_3 form on Ni-Cr and Fe-Cr alloys at chromium levels exceeding 13 and 18%, respectively.[13] The addition of aluminum as well as chromium to iron or nickel also produces an increase in oxidation resistance by the formation of Al_2O_3. Thus, alloys containing chromium and aluminum form continuous protective layers of Al_2O_3 and Cr_2O_3 in an oxidizing atmosphere. However, the protective nature of the oxide layers is somewhat reduced if the chromium oxide layer is above the aluminum oxide layer. The range of partial pressures of oxygen, as calculated from the gaseous mixtures that will be produced in the pilot plant (Tables I and II), is between 10^{-15} and 10^{-17} atm. At these partial pressures of oxygen in the temperature range 700–1100°C, stable oxide layers of chromium that protect against subsequent oxidation of basic alloys can be formed.

Figure 1 shows the thermodynamic stability diagram for the Al-O-S system. The rectangular block in the oxide region refers to the expected range of equilibrium partial pressures of sulfur and oxygen (Tables I and II). As indicated in this figure, Al_2O_3 in a coal-gas environment will be stable at 1000°C, and Al_2O_3 will not transform to Al_2S_3 or $Al_2(SO_4)_3$. Computed diagrams similar to Fig. 1 can also be obtained for higher temperatures, and thermodynamic[14] computations have indicated that Al_2O_3, Cr_2O_3, MgO, and ZrO_2 are stable to 1500°C in coal-gas environments.

Fig. 1. Al-O-S Phase-stability Diagram. Neg. No. MSD-63705.
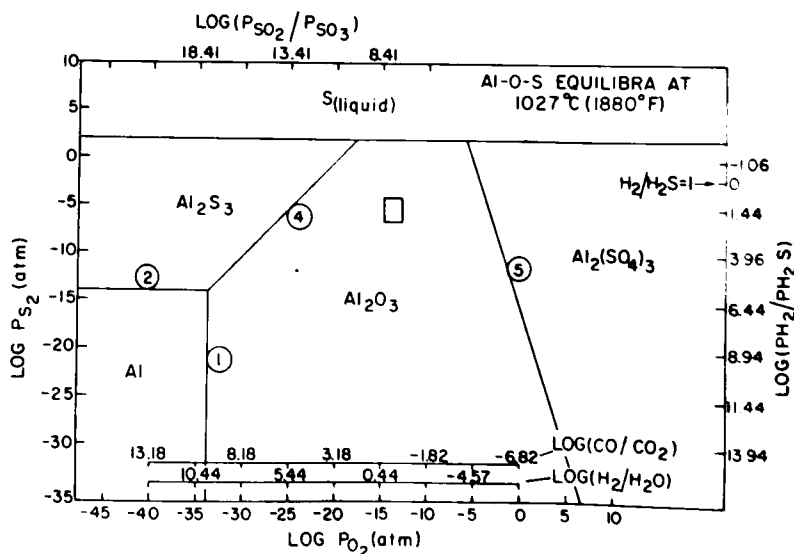
IV. EROSION

The erosion due to the impingement of coal, char, dolomite, or ash particles in the coal-gasification process causes severe wear of components such as cyclones, transfer lines, valves, and pump seatings. This wear is expected to become quite significant because of the simultaneous corrosive attack by coal gas at high temperatures (700-1100°C). The average conditions of corrosion-erosion that are expected to exist in a gasifier at various locations are summarized in Table III. A comparison of these conditions with those existing in aeroturbine engines shows that the particle velocity range is almost 1/10 and particle loading is 10-100 times that for the turbine. Moreover, the gaseous mixture in a coal gasifier is more corrosive than the gases supplied to the turbine engine. The operating temperature range is essentially the same in both cases.

TABLE III. Corrosion-Erosion Conditions
in Coal-gasification Pilot Plants

Gaseous Environments							
	NH_3	CO_2	CO	H_2	CH_4	H_2O	H_2S
(Average vol %)	1	12	18	24	5	39	1

Temperature Range

800-1200°C

Particles

Coal, Char, Dolomite, and Ash (-60 mesh)

Particle Loading

1-30%

Gas Velocity

1.5-30.5 m/s

Angle of Impingement

0-90°

The material loss due to erosive and abrasive actions of impinging particles has been investigated by Finnie.[15] In this analysis, two modes of erosion are distinguished empirically for two classes of materials: a "ductile mode" for metals and alloys and a "brittle mode" for ceramic materials. Figure 2 shows the summary of Finnie's results, which indicates that, for a given particle velocity, the "brittle mode" is characterized by a maximum erosion rate at a particle impingement angle of ≈90°, whereas the "ductile mode" gives a maximum erosion rate at a particle impingement angle between 15 and 30°. Moreover, total erosive wear, which is the case in a coal gasifier, due to particle impingement at various angles could be observed, as shown by the upper curve in Fig. 2.
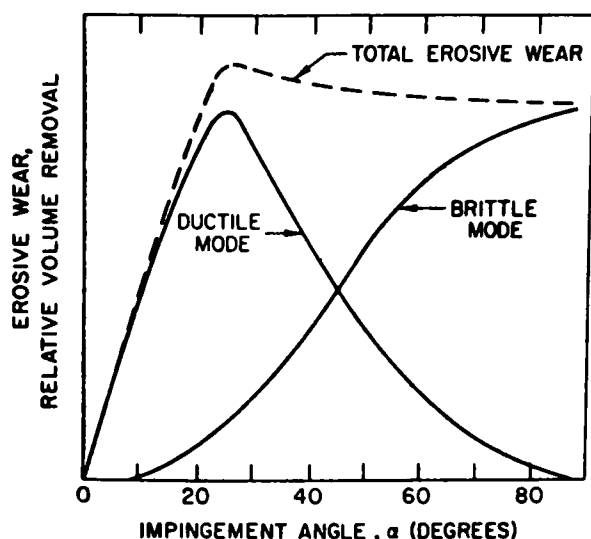
Fig. 2. Erosion Wear as Influenced by Particle-impingement Angle. (From Ref. 15.) Neg. No. MSD-63701.

It should be emphasized that Finnie's analysis predicts erosion wear only at room temperature in the absence of a corrosive environment. Hence, in an actual coal-gasification process, this erosive wear becomes quite complicated since it is influenced by other factors. The study by Smeltzer et al.[16] on the influence of temperature on erosion wear indicates that reduced erosion rates are observed with an increase in temperature, which is contrary to Finnie's analysis. Furthermore, up-to-date experimental erosive-wear work primarily dealt with metals and alloys as target materials; thus, little information is available concerning wear behavior of ceramic materials.

Figures 3 and 4 show the oxidation-erosion data[17] reported by the Allison Division of General Motors for several coating systems on various
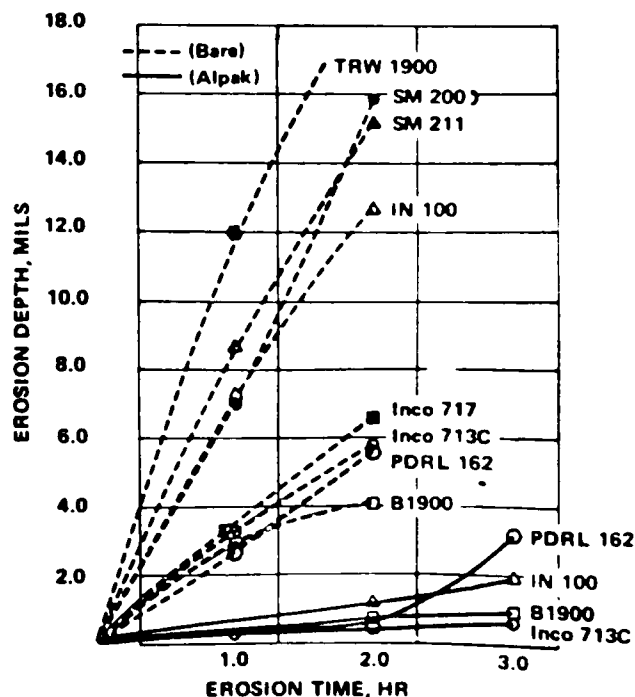
Fig. 3. Oxidation Erosion of Various Bare and Alpak-coated Turbine-blade Superalloys Exposed to 608 m/s Air at 1093°C. (From Ref. 17.) Neg. No. MSD-63703.
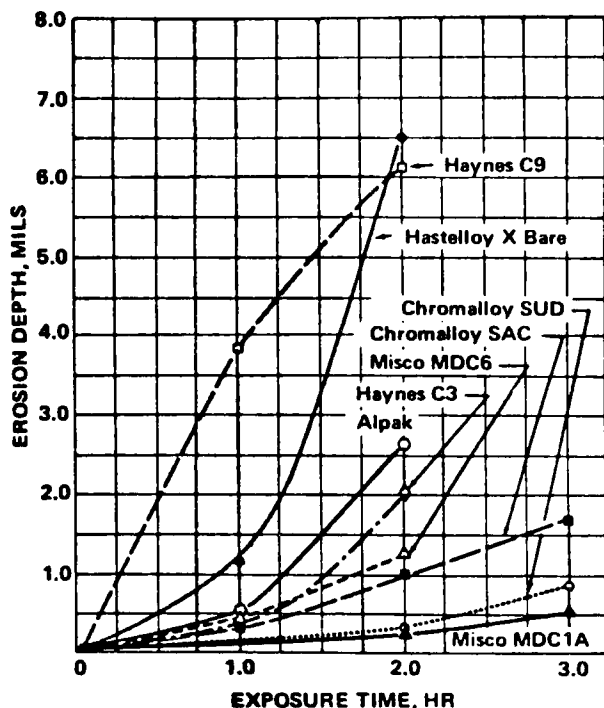
Fig. 4. Oxidation Erosion of Various Commercial Coatings on Hastelloy-X Substrate Exposed to 608 m/s Air at 1150°C. (From Ref. 17.) Neg. No. MSD-63704.

superalloy substrates. The aluminized coatings were applied by the pack-cementation process (as described in Sec. VI.A), which are also known as Alpak coatings. Figure 3 shows the oxidation-erosion results for bare and coated superalloys after they were subjected to high-velocity air (2000 ft/s) at 1093°C. The oxidation-erosion characteristics of various commercial coatings on a Hastelloy-X substrate exposed to high-velocity air (2000 ft/s) at 1150°C are shown in Fig. 4. The following commercial coating systems are compared in Fig. 4: MISCO MDC1A (Al, applied by pack cementation), Alpak, Haynes C9 (Al-Fe, applied by pack cementation), Haynes C3 (Al-Ni, applied by pack cementation), Chromalloy SUD (Al with undisclosed alloying elements, applied by pack cementation), Chromalloy SAC (Al-Cr-Si, applied by pack cementation), and MISCO MDC6 (Cr-Al, applied by an undisclosed process). The Alpak coating on INCO 713C showed minimum oxidation-erosion wear, and good results were also observed for the MISCO MDC1A coating on Hastelloy-X.

V. COATING SYSTEMS

An extensive literature survey indicates that five types of coatings are available which could protect metallic systems at elevated temperatures (a) intermetallic compounds that form compact oxide layers, (b) intermetallic compounds that form glassy oxide layers, (c) alloy coatings that form compact oxide layers, (d) noble metals and alloys that do not react with the environment or react quite slowly to form volatile oxides, and (e) stable oxides that provide a physical barrier to the corrosive environment. Although the present review is concerned primarily with the fifth type of coating system, a brief up-to-date status for each system is given.

A. Intermetallic Compounds as Coatings

The most important protective coatings in this category are aluminides (Ni-Al) on superalloy substrates. The aluminides oxidize preferentially to form a layer of crystalline Al_2O_3 because of the high activity of Al. Al_2O_3 is an excellent protective layer because the rate of diffusion of aluminum cations, from the aluminide substrate through the Al_2O_3 to the surface where it can react with oxygen, is quite low. Transport of oxygen ions through the Al_2O_3 layer is also quite slow. This aluminum oxide film is adherent and has good mechanical characteristics. As long as an aluminide layer is present as a reservoir of Al, mechanical defects in the Al_2O_3 oxide layer are not detrimental. However, mechanical defects in the aluminide layer, which permit the substrate to be exposed, are a source of failure.

If the oxidation resistance of aluminides can be attributed to the formation of a pure or nearly pure Al_2O_3 barrier scale and if a Wagner mechanism is valid,[18] then a minimum of possible oxidation rates are calculable from diffusion data using the following equations:

$$X^2 - X_0^2 = K_p (t - t_0) \quad \text{for a parabolic relation,} \qquad (1)$$

$$X - X_0 = K_l (\log t - \log t_0) \quad \text{for a logarithmic relation,} \qquad (2)$$

where X_0 is an oxide thickness at time t_0, K_p and K_l are parabolic and logarithmic rate constants, respectively, and X is oxide thickness at time t. Pappis[19] studied the self-diffusion of Al in Al_2O_3 at temperatures between 1300 and 1750°C. The results indicated that, in this temperature range, the Al_2O_3 is n-type (oxygen-deficient) at low oxygen pressures ($<10^{-5}$ atm) and p-type (cation-deficient) at high pressures. The self-diffusion data of Al_2O_3 reported in the literature are summarized in Table IV and plotted in Fig. 5. Between 1600 and 2050°C, the aluminum self-diffusion coefficient (D_{Al}) has been observed to be greater than that of oxygen (D_0), and hence, the outward migration of Al is expected to determine the parabolic rate constant in diffusion-controlled kinetics. It is interesting to note that Doherty and Davis[20] demonstrated that crystalline Al_2O_3 at 600°C grows beneath an amorphous film by inward diffusion of oxygen. This mechanism is consistent with the extrapolated relative diffusion rates of Al and O at the lower temperatures (Fig. 5). Hence, simplified equations that would predict a parabolic rate of growth of Al_2O_3 on aluminides that tend to form pure Al_2O_3 scales can be given as

$$X^2 = 4Dt \quad \text{(linear defect concentration)} \qquad (3)$$

and

$$X^2 = 2Dt \quad \text{(uniform defect concentrations).} \qquad (4)$$

In Eqs. (3) and (4), D is the self-diffusion of diffusing specie and is related to the defect diffusivity as $D = D_i \bar{C}$, where D_i is the diffusion of defect specie, and $\bar{C}$ is the average defect concentration.

TABLE IV.   Self-diffusion Coefficients in Alumina

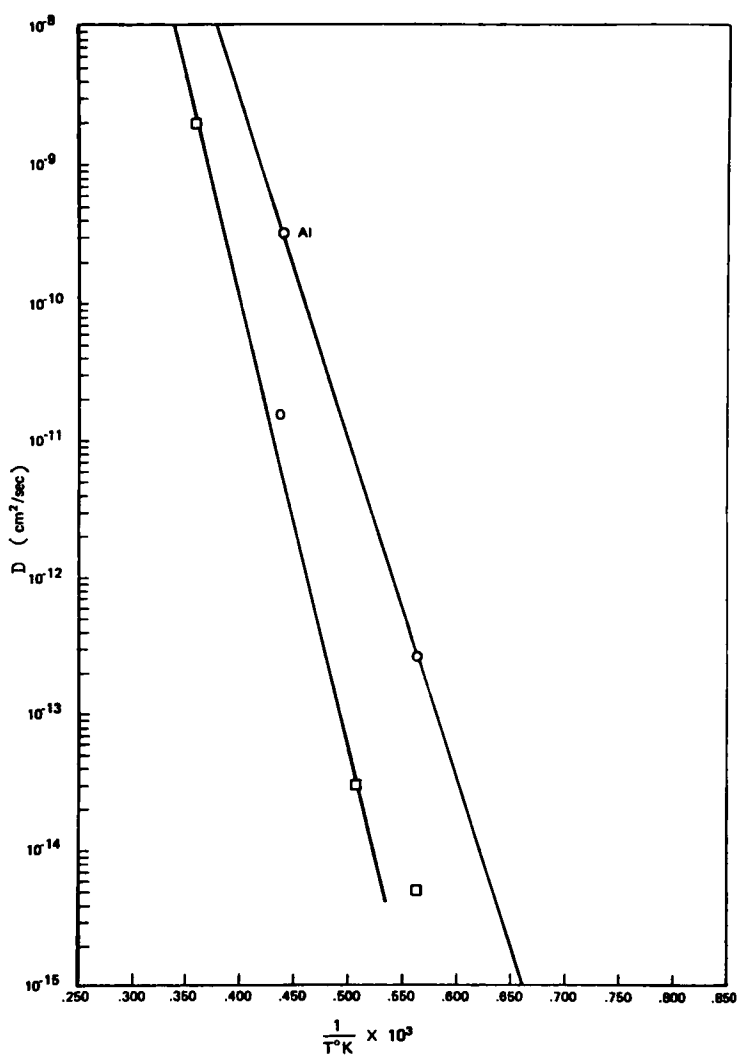| Diffusing Species	D_0, cm^2/s	ΔE_a, cal/mole	Temperature Range, °C
Al	28	114,000	1670-1900
O	1.9×10^3	152,000	>1600
O	6.3×10^{-8}	57,600	<1600

Fig. 5. Self-diffusion in Al_2O_3. (From Ref. 19.) Neg. No. MSD-63700.

Kofstad and Espevik[21] studied the oxidation behavior of a TaAl$_3$-Al coating on tantalum at an oxygen pressure of 0.1 Torr. Preferential oxidation to Al$_2$O$_3$ was observed, and protective behavior was established between 1000 and 1600°C. Below 1000°C, breakaway of the oxide film was observed because of short-circuit diffusion paths.

Many other crystalline oxides, including rare earths, have high melting points and the chemical stability to be potentially useful as oxide reservoirs. In the course of development, these other systems have been tried and, for one reason or another, have failed. The oxides of Ta, Zr, Hf, and Nb do not <u>grow</u> as compact layers during oxidation, thus permitting gaseous transport of oxygen to the substrate. Chromium-rich alloys and compounds produce Cr$_2$O$_3$ layers, but these form volatile CrO$_3$ on further oxidation. The reason for the failure of beryllides to form a useful family of coatings is not yet clear. However, it appears that a large mismatch of volume and thermal expansion between beryllides and metallic substrates is the cause of failure. Also, BeO reacts with water and steam. Crystalline oxides of Ni and Co are not used because metal cation diffusion through the scale is quite rapid.

B. Glassy Oxide Formers as Coatings

Silica is the predominant oxide that can form a glass, although other oxides such as boron oxide might be considered as basic material that can be used to form glassy oxides. The disilicide coatings have been successful for the protection of refractory metal substrates in oxidizing environments (Sec. VII). The silicides of the refractory metals have a number of valuable properties such as resistance to corrosive gases and liquids at high temperatures. The lifetime of these coatings on Nb, Ta, W, and Zr varies between 15 and 70 h when heated in air at 1260°C.

Silica glass coatings have a tendency to lose silicon, through the formation of SiO at low oxygen partial pressure, either by direct dissociation of SiO$_2$ or by reaction with silicon in the disilicide. The loss of SiO$_2$ via SiO or (H$_2$SiO$_3$)$_x$ evaporation will occur rapidly because of the hydrogen and water vapor in the coal gas. Therefore, glassy oxide coatings, especially SiO$_2$, are not suitable in coal-gasification processes.

Diborides form a family of intermetallic compounds that have good oxidation resistance at elevated temperatures. It is possible that the basis for oxidation resistance of the diborides is the formation of B$_2$O$_3$ glass modified with other oxides. Thus far, however, diborides have not been successful as coatings, perhaps because of (1) inadequate techniques to produce them on the substrate, (2) the dissolution of boron into the substrate, and (3) the high volatility of B$_2$O$_3$, which is undesirable in the case of thin coatings. In the present literature survey, it has been concluded that insufficient effort has been expended in the development of diboride coatings to permit an adequate appraisal of their potential.

C. Alloy Coatings (Oxidation-resistant Alloys)

Most of the work in this category is based on oxidation-resistant nickel- and cobalt-base alloys. The basis for oxidation resistance in these alloys is the formation of compact oxides in which diffusion of metal cations

is inhibited. The most desirable oxide layers are those that are sufficiently thin or plastic to avoid mechanical failure during service. Cobalt- and nickel-base alloys for high-temperature application generally contain substantial amounts of chromium. The mechanism for the enhancement of oxidation resistance by chromium appears to be the formation of a $CoCr_2O_4$ and $NiCr_2O_4$ spinel oxide[9-13] layer. The rate-controlling process is believed to be chromium-ion diffusion through the spinel, which is vastly slower than cobalt or nickel ion diffusion through CoO or NiO. An extensive alloy screening in a coal-gas environment is being performed by IITRI[22] and to date their test data at 980°C indicate that only aluminized alloys of IN800 and Type 310 stainless steel have passed the minimum scale loss requirement (<20 mils/year). From these results, it appears that the oxidation resistance offered by the previously mentioned spinels in coal-gas environments is not effective.

D. Noble Metal and Alloy Coatings

The noble metals, particularly platinum and iridium, may be used to protect refractory-metal substrates and graphite.[23] The maximum temperature and time of usefulness can be estimated from the loss of the noble metal by evolution of volatile oxides.[24,25] This loss is strongly dependent on the flow rate of oxygen. Since no mechanism of self-healing is available, the coatings must be perfect to be protective. A secondary concern is interdiffusion of the noble metal into the substrate. Substrate interdiffusion may be avoided through the use of relatively thick barriers of nonreactive oxide. For example, platinum-coated molybdenum and tungsten components are used in the glass-melting technique in which the noble metal is simply a sheath over the refractory metal substrate from which it is separated by an oxide barrier layer, usually Al_2O_3. The noble-metal coating merely serves as a barrier to oxygen and does not contribute structurally. Thus, applications for this system are limited to low stresses where transmission of shear stress across the coating-substrate interface is minimized.

E. Stable Oxides as Coatings

It is generally conceded that the coating systems of greatest promise are those of the reservoir type with a built-in mechanism for repair or self-healing. The aluminides and silicides discussed above are examples of these systems. Serious attention has been paid to spraying or otherwise depositing protective oxide barriers onto the substrates. The oxides of greatest interest are those that exhibit the lowest oxygen-diffusion rates. This assumes, of course, that oxidation resistance will result if the oxygen activity at the substrate-oxide interface is sufficiently low. If the substrate atoms should diffuse rapidly through the outer oxide and become subject to attack at the oxide-gas interface, the efficacy of the entire concept of an oxide barrier could be lost. If the metal ion diffusion through the oxide is negligible or slow, the best possible protection that an oxide barrier can give is determined by the oxygen diffusion through the structurally perfect oxide. Values of oxygen diffusion in a number of refractory oxides are plotted in Figs. 5-7 from data in various studies.[18,26] For exact conditions under which these oxygen diffusion coefficients were determined, refer to the original investigations. Among the single oxides, minimum diffusion rates are found for Al_2O_3 and MgO. These oxides exhibit only small deviations from stoichiometry and have low point-defect concentrations. Zirconia, a stable

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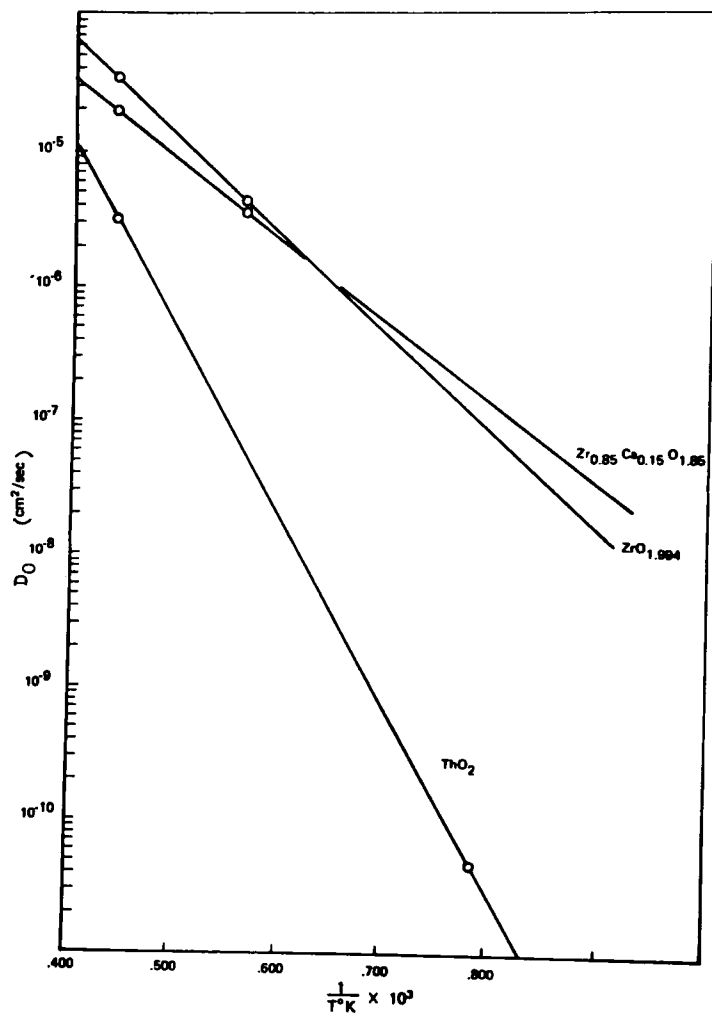
Fig. 6. Oxygen Diffusion in Refractory
Oxides. (Adapted from Refs. 18-26.)
Neg. No. MSD-63698.
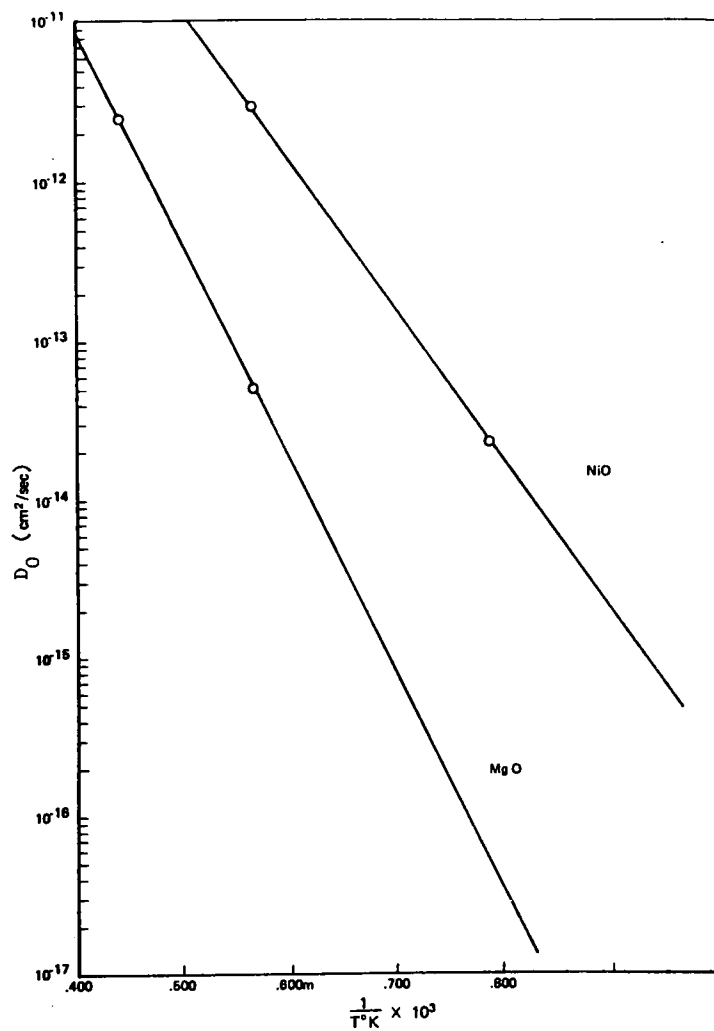
Fig. 7. Oxygen Diffusion in MgO and NiO.
(Adapted from Refs. 18-26.) Neg. No.
MSD-63699.

refractory oxide, generally has a large concentration of oxygen point defects and thus exhibits a greater diffusion coefficient for oxygen than other oxides. The situation could be quite different if the defect concentration could be reduced by some mechanism, such as doping the oxide and thus forming a spinel or perovskite structure. In these structures, cation as well as anion diffusion rates are small.

For an oxide in which nonstoichiometry exists as a result of cation deficiency, the self-diffusion coefficient may play an important role in the protective behavior of the oxide. Figure 8 shows self-diffusion coefficients[17] of cations in various single oxides. The smallest diffusion coefficients are found in CaO, MgO, and Al_2O_3. Oxides such as CoO and NiO do not act as effective barriers against diffusion unless their point-defect concentrations decrease through appropriate cation additions.

In any case, a real question exists concerning the practical utility of a single-layer oxide barrier. Oxides are generally brittle and thus should be deposited as a multilayered structure with or in a suitable metal or alloy matrix. Furthermore, as the diffusion coefficients increase exponentially with temperature, diffusion rates will, at sufficiently high temperatures, become too fast for any oxide to serve as a diffusion barrier. Brett et al.[27] have suggested that oxides should be used as diffusion barriers at temperatures <1900°C, i.e., the protective nature of oxides above that temperature is questionable. Therefore, the practical range of temperature (1000-1200°C) for the use of oxides as protective coatings is well below the upper temperature limit.
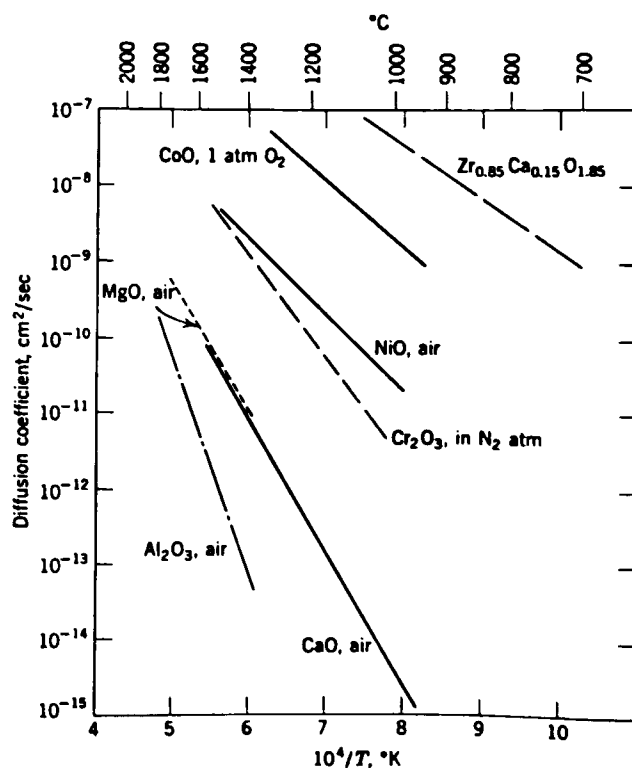
Fig. 8. Diffusion Coefficients for Cations in Oxides. (From Ref. 18.) Neg. No. MSD-63702.

The stability of the oxides in a sulfur-bearing environment that exists in a coal-gasification process should also be considered. Unfortunately, little work has been conducted in this area to determine whether an oxide or mixed oxide acts as a barrier to sulfur diffusion. For nickel-base alloys, Seybolt and Beltran,[28] Bergman et al.,[29] and Donachie et al.[30] observed that corrosive attack in turbine-fuel environments formed NiO, Cr_2O_3, Cr_xS_y, and some spinels such as $Cr_2O_3 \cdot NiO$. The sulfides are usually found in the base alloy and oxide layer. Whether the sulfur penetrates through the oxide by volume diffusion or by some other transport process, the general mechanism of hot corrosion is believed to be due to gradual depletion of Cr, Al, and Ti from the alloy, leaving the matrix nickel rich and more prone to sulfur and oxygen attack. The outer layer of oxide should be impermeable to sulfur diffusion, i.e., compact and stoichiometric oxide should have a negligible sulfur diffusivity to avoid sulfide formation at the oxide-substrate interface. Chang[31] investigated the sulfur diffusion in NiO, CoO, α-Cr_2O_3, and α-Al_2O_3. His results, which are shown in Table V, indicate that α-Al_2O_3 showed minimum sulfur diffusivity. These results further confirm that aluminum oxide as an oxide barrier over the metal substrate should offer a protective layer against sulfur as well as oxygen attack.

TABLE V. S-35 Diffusion Coefficients in
Polycrystalline NiO, CoO, α-Cr_2O_3,
and α-Al_2O_3 at 1000°C[a]

Oxide	D_S (cm^2/s)
NiO	1.0×10^{-11}
CoO	5.2×10^{-12}
α-Cr_2O_3	2.4×10^{-10}
α-Al_2O_3	1.2×10^{-14}

[a] At P_{O_2} of $\sim$1 atm.

VI. COATING MANUFACTURING TECHNOLOGY

Seven manufacturing processes have been used successfully, and a brief description of each will be given.

A. Cementation Process

By far the greatest quantity of coated high-temperature hardware is produced by pack application of diffusion alloy coatings. Pack-coated materials have been predominantly aluminides for the iron-, nickel-, and cobalt-base alloys and simple and complex silicides for the refractory metals.

The basic pack-cementation process[32,33] is accomplished by packing the object to be coated in a powdered mixture consisting of (1) the coating metals or alloys, (2) a halide compound as activator (generally NH_4Cl or

NH_4I), and (3) an inert filler material such as Al_2O_3, MgO, or ZrO_2 to prevent sintering of the powders. In most cases, the reaction chamber (retort) containing the coating ingredients is evacuated or filled with an inert atmosphere to prevent oxidation of the metal powders and the object to be coated. Some processes also use an additional compound (e.g., urea) in the powder mix to control the retort atmosphere. During heating of the retort to a suitable high temperature, the metal or alloy is deposited on the object and diffuses into the substrate. The coatings are solid solutions or intermetallic compounds (or both). They are an integral part of the substrate and have excellent bonding strength.

Some of the coating systems that have been used in superalloys via this process are Cr, Al, Al-Cr, Be, and Al-Cr-X, where X is some additive metal.

B. Slurry Method

The slurry method[34],[35] of applying a coating to the components is advantageous for coating large and reasonably complex shapes. The slurry formed by mixing the coating metals in powder form with some liquid carrier is applied to the substrate by brushing, dipping, or spraying. After the coating suspension has dried, it is given a diffusion anneal in an inert atmosphere (or vacuum) at some elevated temperature. A liquid carrier that will decompose on heating without the formation of an undesirable carbide is generally used. To avoid excessive agglomeration and surface roughness, it is usually recommended that the particle size of the coating metals be relatively small.

Several commercial coatings, i.e., Al, Al-Cr, and Al-Cr-X, where X is a third element, are available that are used primarily for superalloy substrates. The R505, Sn-Al-Mo aluminide, and R512 fused-silicide systems developed by Sylvania have been widely used for Cb and Ta substrates. Solar, Incorporated (Division of International Harvester) has several slurry coating systems for Ta and Cb alloys. In summary, a fairly large commercial capability exists for coating refractory metal hardware with slurry-type coatings, but these processes are restricted to a few suppliers. Only one ceramic and two cermet-type coatings have been developed by Solar and Engelhard Company.

C. Hot Dipping

Hot-dip coatings[33]-[35] are applied by immersing the substrate in a molten bath of a coating metal or alloy that melts at a temperature significantly below that of the object being coated. The molten bath is covered with a flux (frequently halide) to prevent oxidation. The short immersion dip is followed by a diffusion anneal at some elevated temperature. The quality of these coatings is strongly a function of operator skill. For sheet material and wire, the hot-dip process is quite successful and is considered one of the simplest and least costly coating methods. The hot-dip method has been used successfully in applying Al to superalloy and ferrous substrates.

D. Electrodeposition

Electrolytic deposition includes aqueous electroplating, electrodeposition from fused salts, and electrophoresis. The literature survey indicates that aqueous plating has not been explored or is not suitable for forming a high-temperature protective coating. Fused-salt electrodeposition has recently been promoted by General Electric (GE),[36] and several licenses for the GE metallizing process have been issued. This method permits the formation of a wide variety of pure elemental and intermetallic coatings on high-temperature materials. Salt corrosion is a major problem with this process, and some substrate coating combinations are not possible by this method. Dense solid-solution alloys and intermetallic coatings such as borides, silicides, and chromides are formed by this method over Fe-base alloys, superalloys, and refractory alloys.

Vitro Corporation[37] has conducted the major development work on electrophoretic deposition of high-temperature protective coatings over refractory and superalloys. However, major work at the advanced development stage remains. The flexibility of this process[38] for the application of uniform deposits of complex alloys or intermetallics (such as Al-Ni, Al-Cr, Mo-Si, and WSi) to irregular shapes makes it particularly attractive, especially for those types of alloy coatings not amenable to formation by a diffusion growth process. This process has been used widely for the coating of refractory metal fasteners.

E. Vapor Deposition

1. Chemical

Chemical vapor deposition (CVD),[34,35,39] also referred to as vapor plating or gas plating, is a method whereby a volatile form of the compound to be deposited is brought in contact with a heated substrate. The desired coating is built up in molecular steps via either displacement reduction or thermal decomposition reactions of the plating compound at the surface of the work piece. Producing a desired coating by CVD requires that the coating metal exist as a compound which can be readily vaporized at a relatively low temperature without thermal degradation. Also, it must be sufficiently unstable at some elevated temperature to be reduced or pyrolized to the desired metal with minimum side reactions. A wide variety of such compounds exist, ranging from several halides to various organometallics.

The CVD processes, with proper selection of starting materials, can be used to produce dense coatings. However, the prerequisite thermodynamics and kinetics studies have been done for only a small number of pertinent reactions. Hence, the technology of CVD is at a preliminary stage of development. Chromizing, aluminizing, and siliconizing by CVD have been demonstrated, both with and without subsequent diffusion heat treatments. Both silicon and SiC coatings have been applied to graphite using CVD techniques. It can be seen from Table VI that a variety of deposits, such as Si, SiC, BN, NbC, Al_2O_3, ZrO_2, HfO_2, and refractory-metal coatings, have been attempted at the laboratory scale using CVD techniques. However, most of these coatings have not been utilized to coat hardware, with the exception of refractory metal

TABLE VI. Summary of Important Coating Processes

Process	Number of Steps	Coating Materials	Substrate Materials	Atmosphere	Remarks
Pack Cementation	1 or 2	Al,Al-Cr,Al-Cr-X	Superalloys, refractory metals, or alloys	Inert, halide (both in sequence)	No special holding fixture required. Long heat-up and cool-down times required. Coatings are diffusion bonded, thin, and reasonably uniform.
Slurry	Multiple	Al,Al-Cr,Al-Cr-X	Superalloys, refractory metals, or alloys	Inert, vacuum	Avoids long heat-up and cool-down times. Needs special holding fixture. Coatings are diffusion bonded, thin, dense, and reasonably uniform.
Hot Dipping	Multiple	Al,Al-Cr	Ferrous, nickel-base alloys	Flux or inert	Short reaction times. Process is basically limited to Al or Al-X type coatings. Coatings are diffusion bonded, reasonably dense, and nonuniform.
Electrodeposition					Intricate shapes can be coated by this method.
Fused Salt	1 or more	Produces -iding coatings (e.g., berylliding, titaniding)	Any metal with melting point above 1200°F	Chloride or fluoride bath	Cumbersome method but produces dense and uniform coating.
Electrophoretic	Multiple	Al-Ni,WSi$_2$,MoSi$_2$, Al-Cr,borides[a]	Ferrous superalloys, refractory alloys	Both	Coatings are relatively porous. Process is mainly in development stage.
Vapor Deposition					
Chemical	2 or more	W-Mo,Ni,Ti,Cr,Al$_2$O$_3$, HfO$_2$,ZrO$_2$,BN,SiO$_2$, Ta$_2$C,SiC,Si$_3$N$_4$,TaC[a]	Refractory metals, graphite, some on Ni- and Fe-base alloys	Vacuum or inert	Special holding fixtures required. Coating up to 95$^+$% dense could be produced. Complicated equipment required. Process is mainly in development stage.

Physical
    Vacuum Vaporization
    Sputtering
    Ion Plating
	1 or 2	All metals, some ceramics
		Metals, ceramics[a]
		Alloys, metals, some ceramics[a]
			Metal, alloy, or non-metallic substrates	Vacuum or inert partial pressure	Ion plating combines the processes of vaporization and sputtering; produces excellent dense, adherent, and uniform coatings due to excellent throwing power. Ion plating is in development stage and has been used for coating small components only.

Vitreous or Glass Refractory	Multiple	Oxides only	Fe- and Ni-base alloys	Air or inert	Thermal stresses at the interface impose a problem. Process produces thick coatings (~100 mils) and is inexpensive.
Plasma Spray	1 or more, depending upon coating system	Metal, alloy, aluminides, silicides, ceramics, cermets, plastics, intermetallics	Metal alloys, ceramics, plastics	Air or vacuum	Coatings are uniform but contain slight porosity (4-15%). Method is inexpensive and can be used at plant sites.

[a]Only in development stage, i.e., not available on commercial scale.

coatings applied to rocket nozzles and tubing. The companies that developed
CVD techniques for these deposits were Fansteel (San Fernando Laboratories),
Union Carbide, Sylvania, and General Technologies. The main disadvantage of
the CVD process is that it requires complex equipment and produces coatings
of medium quality.

2. Physical

Physical vacuum vapor deposition (PVD)[35,40,41] encompasses methods of
applying a coating that involve physical evaporation of a coating-material
source and line-of-sight condensation of this vapor phase on the surface to
be coated. Vacuum evaporation, sputtering, and ion plating are common termi-
nology for vacuum vapor-deposition processes. In these processes, chamber
pressures of the order of 10^{-4} to 10^{-7} Torr are required. For evaporation
and ion plating, the source coating material is heated by resistance, induc-
tion, electron beam, or other means to promote evaporation. The rate of
evaporation is controlled by the temperature and pressure conditions. The
substrate to be coated may be heated during deposition to enhance diffusion
bonding of the coating to the substrate. In the case of sputtering, a plasma
discharge in a partial pressure of inert gas (argon or helium) is created,
and thus the positively charged argon ions dislodge the coating material
(target), which, in turn, condenses on the substrate. For ion plating, both
evaporation and sputtering are occurring simultaneously, and hence, vapor
ions are accelerated through the discharge and deposited on the substrate with
an impingement energy of 1-3 keV.

The methods described above have been used primarily for the deposition
of thin-film coatings on, for example, mirrors, semiconductor products, and
camera lenses. Little work[42] has been done to apply these techniques to
deposition of from 1- to 4-mil-thick protective coatings on high-temperature
materials. In the last three to four years, Pratt and Whitney, GE, and
Temescal, Inc. have coated superalloy components (vanes and blades) with
Fe-Cr-Al-Y and Co-Cr-Al-Y using sputtering and evaporation techniques.

For the three PVD methods, relatively sophisticated vacuum equipment
is required, and a great deal of effort is needed to develop manufacturing
methods applicable to large components. However, these techniques have shown
the feasibility of producing up to 25-µm-thick thin films of alloy as well as
ceramic materials.

F. Vitreous or Glassy-refractory Technique

High-temperature vitreous or glassy-refractory coatings are applied
to Fe- and Ni-base alloys by using modifications of existing enameling
methods.[34,35,43] Vitreous coatings are smooth, nonporous bonded, and resis-
tant to temperatures up to 1000°C for long periods. Improvements in vitreous
coatings are made by adding refractory oxides (e.g., ZrO_2 and Al_2O_3) to the
basic coating formulation. This addition can protect the substrate up to
1200°C. The frits of proper composition are powdered, mixed, and slurried.
This slurry is applied to the substrate and air dried. The coating is pro-
duced by firing in air at some elevated temperature from 1 to 30 min. Vitreous
coatings are usually fired at 560-870°C, whereas glassy-refractory coatings
are fired above 815°C.

The main disadvantage of this coating is that high stresses are produced at the interface, and hence thermal-shock resistance of a coating-substrate system is quite poor. However, the process is inexpensive and could be useful for large components, provided some graded structures of metallic-oxide mixture type could be coated as an intermediate layer.

G. Plasma Spraying

Plasma-spray techniques[44] involve the physical deposition of the coating material on the surface by a plasma-arc process. The coatings produced by the plasma-spray method are in wide use as hard-wear and corrosion-resistant materials applied to contacting or rubbing surfaces of iron-, nickel-, and cobalt-base alloys. This method employs a direct-current arc (up to 80 kW) to ionize flowing gases (e.g., argon, argon-hydrogen, or helium) that also contain the coating materials in the form of fine powder. A variety of materials such as metals, alloys, oxides, carbides, borides, aluminides, and cermets can be plasma sprayed to produce coatings resistant to high-temperature wear, fretting erosion, abrasion, and corrosion. In general, plasma-spray coatings have not exhibited corrosion-resistant properties equivalent to diffusion coatings; however, 95$^+$% dense ceramic and cermet coatings have been produced by a high-energy plasma gun, which has resulted in improved corrosion resistance of the coatings. Another major advantage of a ceramic coating produced by this method is that a graded cermet-to-ceramic coating can be plasma sprayed to reduce the thermal stresses. The coatings produced by this method have better thermal spalling resistance than those produced by the vitreous method. Since the composite material compositions (various ceramics and cermets) are virtually unlimited, the primary developmental effort should be directed at the utilization of these methods for the production of a coating not amenable to formation by diffusion growth processes. Complex iron, nickel, and cobalt alloys, intermetallics and borides have demonstrated excellent corrosion resistance, but their fabrication by conventional methods has not been successful. Therefore, plasma-spray techniques have been explored and developed to deposit materials such as dense (up to 90%), adherent, and thick coatings over various components used in space programs.[45,46]

VII. MATERIALS AND COATING TECHNOLOGIES FOR STRUCTURAL COMPONENTS

The recommendations for ceramic coatings that can be used in the coal gasifier and the developmental areas are discussed. Only certain coating manufacturing techniques are worthy of exploration to produce dense, uniform, and adherent ceramic coatings.

A. Ceramic Materials

High-temperature ceramic compounds are worthy of consideration for coatings, provided they offer good resistance to scaling and good adherence to the substrate. The protective capacity of an oxide layer may be estimated by the Pilling-Bedworth (P-B) ratio, which relates the specific volume of the oxide formed to the specific volume of the corresponding metal. The P-B ratio (α) is given as

$$\alpha = M \cdot d / m \cdot D \, , \qquad (5)$$

where M is the molecular weight of the oxide (or mixture in the case of mixed oxides) formed upon oxidation of 1 g-mole of compound, m is the molecular weight of the oxidized compound, and D and d are the densities of the oxide and compound, respectively.

For $\alpha < 1$, the film is discontinuous, resulting in continuous oxidation, whereas for $\alpha > 1$, a protective oxide layer is formed that inhibits the access of oxygen under known conditions (parabolic law). For large values of α, the layer has considerable internal stresses, spalls, and loses its protective properties; therefore, the best protective properties are possessed by layers for which α does not greatly exceed unity. Data[47] on the values of α for the carbides, borides, and nitrides of some refractory metals are given in Table VII.

TABLE VII. Pilling-Bedworth Ratio
for Some Ceramic Compounds

Carbide[a]	α	Boride[a]	α
TiC	1.53	TiB_2	1.21
ZrC	1.43	ZrB_2	1.16
NbC	2.22	NbB_2	1.71
TaC	1.91	TaB_2	1.48
WC	2.72	Mo_2B_2	2.19
Mo_2C	2.72	W_2B_5	2.11
SiC	1.71		
		Oxide[b]	
Nitride[a]		Al_2O_3	1.28
TiN	1.57	Cr_2O_3	2.07
ZrN	1.41	ZrO_2	1.45
NbN	2.25		
TaN	1.84		
Mo_2N	2.5		
WN	2.09		
Si_3N_4	1.65		

[a]Ref. 47.

[b]Ref. 48.

The P-B ratio has the lowest values for the carbides and nitrides of Ti, Si, and Zr, and the highest value for compounds of W and Mo. Accordingly, the carbides and nitrides of Si, Zr, and Ti should have the highest resistance to scaling and those of Mo and W the lowest. The relatively satisfactory resistance to scaling for the carbides and nitrides of Ti, Zr, and Si is also due to the fact that a pseudomorphous layer[*] of a solid solution of a lower

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[*]A pseudomorphous layer is a thin layer adjacent to the underlying matrix, the lattice of which has orientational correspondence with and similar lattice constants to the lattice of the matrix.

(or normal) oxide in the carbide or nitride (such as TiC-TiO, SiC-SiO$_2$, etc.)
is formed at the interface between the compound and oxide layers.[49] The pro-
cess of formation and growth of the pseudomorphous layer slows the oxidation
process of the compound. The oxides of Mo and W have high volatility at high
temperatures, and a protective oxide layer is never formed. For carbides and
nitrides of Ta and Nb, lower oxides with nonisomorphous characteristics are
formed. These pseudomorphous layers are unstable, which results in a high
rate of oxidation compared with carbides and nitrides of Zr and Ti.

During the oxidation of borides, volatile boric anhydride and oxides
of the corresponding metals are formed. The solubility of the oxides of most
metals in boric anhydride is low, and therefore the formation of pseudomor-
phous layers with their protective character is not expected. However, the
corrosion protection offered by the oxides of boride compounds depends upon
two properties: the evaporation of boric anhydride and the formation of
borates. The only two compounds that could provide good resistance to scaling
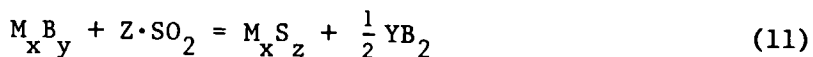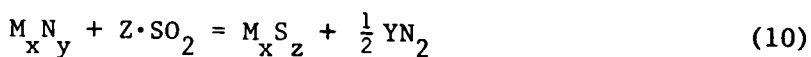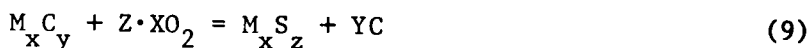are TiB$_2$ and ZrB$_2$.[50]

In addition to the P-B ratio (α) for the compounds given in Table VII,
one should also consider the stability of these compounds in coal-gas environ-
ments such as that given in Table I. With the given oxidizing and sulfiding
partial pressures, the following types of reactions could take place:

$$M_xC_y + Z \cdot O_2 = XMO_2 + YCO_2 \uparrow \tag{6}$$

$$M_xN_y + Z \cdot O_2 = XMO_2 + YNO_2 \uparrow \tag{7}$$

$$M_xB_y + Z \cdot O_2 = XMO_2 + \tfrac{1}{2} YB_2O_3 \tag{8}$$

or

$$M_xC_y + Z \cdot XO_2 = M_xS_z + YC \tag{9}$$

$$M_xN_y + Z \cdot SO_2 = M_xS_z + \tfrac{1}{2} YN_2 \tag{10}$$

$$M_xB_y + Z \cdot SO_2 = M_xS_z + \tfrac{1}{2} YB_2 \tag{11}$$

or

$$aM_xC_y + Z \cdot O_2 + P \cdot SO_2 = XM_a(SO_4)_b + aYCO_2 \uparrow \tag{12}$$

$$aM_xN_y + Z \cdot O_2 + P \cdot SO_2 = XM_a(SO_4)_b + aYNO_2 \uparrow \tag{13}$$

$$aM_xB_y + Z \cdot O_2 + P \cdot SO_2 = XM_a(SO_4)_b + \tfrac{a}{2} YB_2O_3. \tag{14}$$
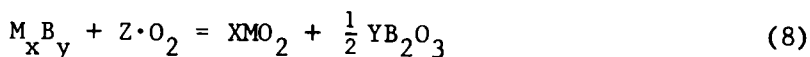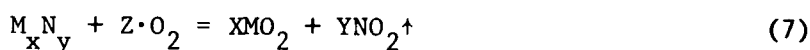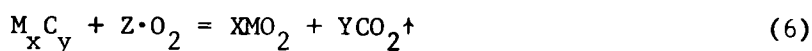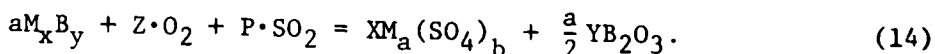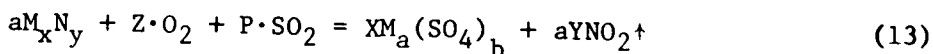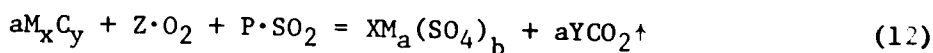
Depending upon the partial pressures of the reactants in the gaseous
mixture, any of the above reactions will proceed toward the right if the free
energy of reaction [$(\Delta G)_R$] is negative. Table VIII gives the $(\Delta G)_R$ of oxida-
tion and sulfidation reactions for selected ceramic compounds. It is encour-
aging to note that most of the compounds (or coatings), except for chromium

TABLE VIII. Free Energy of Reactions[a] in a
Coal-gas Mixture at 1026°C

Ceramic Coating	$(\Delta G)_R$ at $P_{O_2} \simeq 10^{-16}$ atm, kcal/mole	$(\Delta G)_R$ at $P_{S_2} \simeq 10^{-5}$ atm, kcal/mole
B_4C	-165	+209
TiC	-137	+10
SiC	+133	+20
BN	-31	+110
TiN	-28	+22
Si_3N_4	-149	+87
TiB_2	-94	+39
Al_2O_3	+332: $Al_2(SO_4)_3$	+83
ZrO_2	: $Zr(SO_4)_2$[b]	+40
MgO	+96: $MgSO_4$	+96
Cr_2O_3	+860: $Cr_2(SO_4)_3$	+34
Cr_3C_2	-107	-32

[a]See reactions (6)-(14).

[b]Thermodynamic data not available.

carbide, will resist sulfidation attack. Furthermore, all listed compounds (except for SiC) form an oxidized layer that will act as an oxygen reservoir for base metals and thus will protect against subsequent oxidation. Silicon carbide will not oxidize at $P_{O_2} = 10^{-16}$ atm and a temperature of 1026°C. Singhal[51] demonstrated that both fully dense SiC and Si_3N_4 (at 1200°C) exhibited much less surface degradation after a 250-h exposure to combustion gases containing sulfur, sodium, and vanadium. An extensive investigation of the oxidation behavior of SiC and Si_3N_4 compounds has been performed.[52-54] Oxides such as Al_2O_3, ZrO_2, and Cr_2O_3 will not be converted to the corresponding sulfide or sulfate in the coal-gas environments listed in Table I.

The resistance to high-temperature oxidation of silicides is accomplished by the formation of refractory metal silicides, which have been investigated by Samsonov.[55] The formation of a protective coating and its stability depends upon the volatility of the oxide layer and the uniform growth of the vitreous layer of SiO_2, as shown by the following reactions:

$$MSi(MoSi_2, WSi_2) + xO_2 \rightarrow MO\uparrow(\text{volatile}, MoO_3, WO_3) + SiO_2, \qquad (15)$$

and

$$MSi(CrSi_2, ZrSi_2, TiS_2, VSi_2) + xO_2 \rightarrow MO(\text{nonvolatile},$$
$$Cr_2O_3, ZrO_2, TiO_2) + SiO_2. \qquad (16)$$
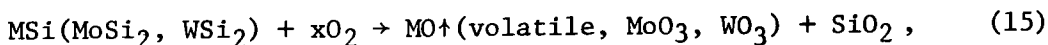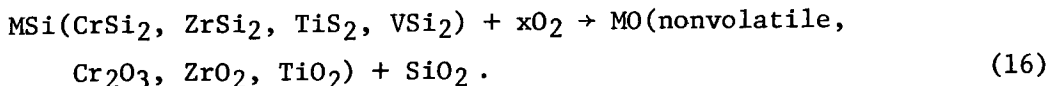
In reactions (15) and (16), it is essential that the SiO_2 vitreous layer be formed rapidly to protect the substrate character. In the case of volatile oxide formation, metal will be consumed until a protective layer of SiO_2 is formed.

However, above 800°C, the presence of steam and hydrogen in the coal-gas composition will reduce SiO_2 following the reactions[56,57]

$$SiO_2 + H_2 \rightarrow SiO\uparrow + H_2O \text{ (steam)} , \qquad (17)$$

and

$$SiO_2 + H_2O \text{ (steam)} \rightarrow H_2SiO_3 . \qquad (18)$$

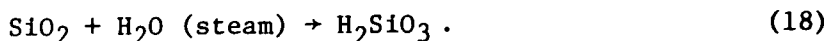Thus, the protective character of silicide compounds is possible in pure oxidizing or oxidizing plus sulfiding environments. However, in a coal-gas environment, they would offer poor protection for the substrates.

B. Coating Adherence

The adhesion of ceramic coatings to the metal substrate is another critical phenomenon that cannot be ignored in this review. The adhesion strength of an interface is a measure of the degree to which the two surfaces are attracted. The adhesion of coating is dependent on (1) the condition of the metal surface, and (2) the condition (or method) of coating material when it hits (or impinges) the metal surface. The interfacial stresses (or residual strains) will be different for a substrate-coating system, depending upon the method of producing the coating. Bryant and Ammon[58] and Goechius and Bryant[59] made several significant contributions to the understanding of residual strains in coatings.

Ceramic coating-metal composites are in many respects parallel laminates. When the composites of this type are cooled from the temperatures at which the coatings have been produced, residual stresses develop in the system. Considering the composite system as isotropic, Lauchner and Bennett[60] developed a biaxial stress model from the elastic behavior of the components. They derived a mathematical relation for residual stresses (σ_r) in the coating as

$$\sigma_r = \left[\int_{t_a}^{t_c} (\alpha_2 - \alpha_1) \, dt \middle/ \left(\frac{1}{E_2} \cdot \frac{2A_1}{A_2} + \frac{1}{E_1} \right) \right] \cdot \frac{1}{(1 - \mu)} , \qquad (19)$$

where α_1 and α_2 are the coefficients of thermal expansions for the coating and the metal substrate, respectively; E_1 and E_2 are the moduli of elasticity for the coating and metal substrate; A_1 and A_2 are the areas, respectively; μ is Poisson's ratio; and t_a and t_c are, respectively, ambient and hypothetical no-strain temperatures.

An external stress is induced in the coating-substrate system if the latter is quenched from a high temperature. When considering a coating-metal

system of appreciable coating thickness, the maximum thermally developed stress (σ_t) then may be expressed as[61]

$$\sigma_t = \frac{E}{1 - \mu} \cdot \int_{t_a}^{t_s} \alpha(t) \, dt \, , \tag{20}$$

where

$$t_s = t_a - k \beta (t_a - t') \, . \tag{21}$$

Combining the residual and thermally developed stresses, the critical fracture stress (σ_f) for a substrate-coating system is

$$\sigma_f = \sigma_t + \sigma_y = \frac{\displaystyle\int_{t_a}^{t_c} (\alpha_2 - \alpha_1) dt}{\dfrac{1}{E_2} \cdot \dfrac{2A_1}{A_2} + \dfrac{1}{E_1}} \cdot \frac{1}{(1 - \mu)} + \frac{E_1}{(1 - \mu)} \int_{t_a}^{t_s} \alpha(t) \, dt \, , \tag{22}$$

where t' and t_s are, respectively, quenching medium temperature and surface temperature, β is heat-transfer ratio = $r_m h/k$; k is thermal conductivity, h is coefficient of heat transfer, and r_m is normal distance from surface to midplane.

Lauchner and Bennett[60] investigated four types of ceramic coatings over a metal substrate. On the basis of the mathematical treatment and the observed data, they concluded that (1) the ceramic coatings which received a given thermal treatment fracture when thermally shocked by a critical temperature differential, (2) in the absence of residual coating stress, thermal-shock resistance is inversely related to the thermal-expansion characteristic of the coating, (3) the critical stress at which coating fracture may be expressed as the sum of thermal and residual stresses developed in an annealed system in which viscous or plastic flow does not occur, (4) the residual compressive stress in a coating is a desirable factor to improve thermal-shock resistance, and (5) the thermal-shock resistance is improved as the coating thickness decreases.

Hecht[61] investigated the adherence mechanism in plasma-sprayed coatings using alumina and zirconia materials. Most of the ceramic particles are completely molten on impact from a spray distance of 2 to 2.5 in. and at a gun power of 13.75 kW. Because of the rapid quench rate of coating particles, limited or negligible atomic diffusion into the metal occurs. This limited diffusion inhibits interparticle sintering and intermediate compound formation. Therefore, it is important that the impacting particles are as fluid as possible for maximum interfacial contact among particles and between particles and substrate. The increase in interfacial contact between particles increases the surface regions available for localized diffusion (sintering)

and fusion (recrystallization from the melt) as well as for physical attraction (Van der Waals forces). It was inferred[61] that all three of these mechanisms contribute to interparticle cohesion.

Recently, Dapkunas[62] and Swaroop[63] explored the effect of interfacial stresses between ceramic coatings and metal substrates for various systems. Primarily Dapkunas[62] investigated adherence of zirconia-base coatings to superalloys, whereas Swaroop[63] and Swaroop and Fousek[64] investigated ceramic coatings, i.e., Al_2O_3, Cr_2O_3, $MgO \cdot Al_2O_3$, and $MgO \cdot ZrO_2$, on stainless steels (Types 310, 304, and 316) and Incoloy 800. It was observed that an improved adherence and thermal-shock resistance could be obtained in the case of graded zirconia-base coatings in contrast to graded Al_2O_3, Cr_2O_3, or $MgO \cdot Al_2O_3$ coatings. These systems were thermal-shock tested[65] from 1000°C in a steam (or air) environment to room temperature.

The erosion and abrasion properties of a compound are directly related to the hardness of the compound. In general, the erosion properties of the coating are better if the coating material is harder. Table IX lists the microhardness of the selected alloys, metals, and ceramic compounds. The microhardness of ceramic compounds is greater than that for alloys and metals. Furthermore, the microhardness of the silicides is much less than that of the carbides, nitrides, and borides.

TABLE IX. Microhardness[a] of Various Metals, Alloys, and Ceramic Compounds

Metal	Micro-hardness	Carbides	Micro-hardness	Borides	Micro-hardness
Fe	110	TiC	3000	TiB_2	3370
Ti	160	ZrC	2930	ZrB_2	2250
Zr	97	HfC	2900	HfB_2	2900
Hf	200	NbC	1960	NbB_2	2600
V	65	TaC	1600	TaB_2	2500
Nb	88	Mo_2C	1500	CrB_2	1780
Ta	100	W_3C	1800	W_2B_5	2660
Cr	150	Cr_3C_2	1350		
Mo	190	SiC	2500	Silicides	
W	350			$TiSi_2$	8900
		Nitrides		$ZrSi_2$	1060
Alloys[b]		TiN	1900	$HfSi_2$	930
304SS	160	ZrN	1480	$NbSi_2$	1050
310SS	190	HfN	1640	$TaSi_2$	1400
316SS	780	NbN	1400	$CrSi_2$	1130
IN800	155	TaN	1060	$MoSi_2$	1200
1020CS	150	CrN	1080	WSi	1070
		Si_3N_4	1950		
				Oxides	
				Al_2O_3	3000
				Cr_2O_3	2200
				ZrO_2[c]	1470

[a]Knoop hardness in kg/mm^2. [b]Annealed sheet material. [c]Stabilized 10% CaO.

In view of the properties of various ceramic compounds, it is concluded that silicides offer no protection against reducing, sulfidation, or erosion (or abrasion) under conditions that exist in coal gasifiers. Many ceramic compounds can be used as coatings that could offer protection against oxidation and sulfidation up to 1200°C and could also meet the challenge of erosive wear due to char, ash, or dolomite particles in the coal-gas environment. These prospective candidate materials are listed in Table X. The materials are recommended on the basis of chemical and physical properties that are desirable in coal-gasification processes.

TABLE X. Recommended Ceramic Compounds for Coatings

Oxides	Carbides	Nitrides	Borides
Al_2O_3	SiC	Si_3N_4	TiB_2
Cr_2O_3	B_4C	ZrN	ZrB_2
ZrO_2[a]	ZrC	TiN	HfB_2
MgO	HfC	HfN	
$MgO \cdot Al_2O_3$	TiC	BN	
$MgO \cdot ZrO_2$			

[a]Stabilized (preferably with yttria).

The thermal spalling resistance of a coating-metal substrate system is generally quite poor because of the mismatch of thermal expansion between the ceramic coating and the metal substrate. Therefore, to combat this problem, these ceramic coatings should be applied on the metal substrate in a gradual compositional gradient from the metal-rich matrix at the metal interface to ceramic-rich at the top. Such methods have been developed over the past five to seven years.

It should be mentioned that diffused coatings (pack-cementation type) of intermetallic compounds (e.g., nickel-aluminides) have been used in protecting Fe-, Ni-, and Co-base alloys under the fuel environment that exists in a turbine engine. The performance of these coatings has been poor and, hence, FeCrAlY and CoCrAlY coatings were developed to combat the hot-corrosion problem. It is recommended that some of the FeCrAlY and CoCrAlY coatings should also be explored with respect to their stability, integrity, and protective potential under a coal-gas environment in which hydrogen sulfide (or sulfiding potential) is present in larger amounts than in turbine fuel or exhaust gases.

C. Manufacturing Techniques for Ceramic Coatings

Reviewing Sec. VI, it is apparent that four techniques are feasible for producing ceramic materials as coatings: (1) chemical vapor deposition; (2) physical vapor deposition, vacuum evaporation, sputtering, and ion plating; (3) vitreous or glassy-refractory technique; and (4) plasma spraying.

To date, the CVD technique has been successful for a few ceramic coatings such as SiC, Si_3N_4, TaC, HfO_2, ZrO_2, Al_2O_3, and BN. The technique is still in an advanced development stage, except that it has reached commercial usage for small, semiconductor components. As explained earlier, the technique involves heating the substrate to a high temperature (between 400 and 1100°C). No doubt this technique has produced dense and adherent coatings. However, the CVD technique has not been developed to the stage that can directly be applied to coat large or medium size components. At least five to eight years will be required before CVD can be used commercially for coating large components. This time interval is uncertain as it depends upon the magnitude of effort involved in the developmental work.

Of all the PVD methods (modified sputtering), ion plating has shown quite promising results in producing dense, adherent, uniform ceramic coatings. Again, this technique is also in the development stage; however, one advantage is that in PVD, in contrast to CVD, a heated substrate is not required for the primary reaction. Moreover, coatings produced by PVD are of superior quality.

The vitreous or glassy-refractory technique is the most economical process for producing only oxide coatings on metal substrates. Carbide, nitride, or boride coatings cannot be produced by this technique. Furthermore, the component must be fired (or heated) to a high temperature (>900°C) to form an overlay of oxide. It is recommended that this process should be explored with regard to oxide coatings on iron- and nickel-base alloys and the production of gradient-oxide coats to avoid thermal stresses.

The plasma-spray technique has been used commercially for the past 15-20 years and can provide a dense (up to 95%) and uniform coating of various ceramic materials. This technique is relatively low cost and can be used at the site to coat large components. Furthermore, improvement in quality of ceramic coatings is expected because of the advent of a high-energy plasma gun.

The technology to produce graded coats of ceramics with metal or alloy has been developed to its commercial application. It should be mentioned that the plasma-spray technique is presently being used commercially to produce oxide and carbide (three types) coatings. However, to produce coatings of nitrides and borides, developmental work is needed.

A comparison of the relative merits of the techniques capable of producing ceramic coatings is found in Table XI. These are only the author's recommendations; therefore, depending upon a particular need, any one of these techniques should be explored to its maximum capability.

VIII. CONCLUSIONS

The state-of-the-art survey of coating technology indicated that ceramic compounds of the type Al_2O_3, ZrO_2, or Cr_2O_3; SiC, HfC, or ZrC; Si_3N_4, TiN, or HfN; and TiB_2, ZrB_2, or HfB_2 have the desirable properties that could offer corrosion-erosion resistance to the coal-gas (char) mixture at temperatures between 800 and 1200°C. These compounds should be used to form the overlay coating structure on the metal components and should be mixed (or

TABLE XI. Suggested Manufacturing Techniques for Ceramic Coatings

Technique	Coating Capability	Relative Cost	Present Status[a]
Plasma Spray	Offers maximum number of ceramic materials	Relatively in-expensive	C
Ion Plating (PVD) (Sputtering)	Oxides, carbides, nitrides	Initial capital expenses for equipment	D
CVD	Oxides, carbides	Initial capital expenses for equipment. High operational cost	D
Vitreous Refractory Coatings	Oxides only	Relatively in-expensive	C

[a] C refers to commercial and D refers to developmental.

graded) with suitable alloy or cermet materials so that thermal-expansional mismatch between the metal substrate and ceramic overlay is reduced. This technique should produce a tough matrix for good erosion resistance. Furthermore, coating structures of mixed oxides, carbo-nitrides, or mixed borides should be explored to take advantage of the chemical inertness of one compound and the hardness of another.

The survey of various methods of producing coating indicated that the plasma-spray technique has been developed to the stage such that quite a number of ceramic compounds could be coated on the commercial components. The techniques such as sputtering, ion plating, and chemical vapor deposition could produce adherent and dense ceramic coatings. However, these need extensive developmental work for use on a commercial scale for the large components in coal-gasification plants.

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